Predictions confirmed for shift reaction in supercritical water

Dick Steeper and Steve Rice have confirmed the predictions of theoretical work that describes the water density dependence of the conversion of CO and H_2O to CO_2 and H_2 in supercritical water.

Recently, it has become apparent during the development of oxidation models in high-pressure environments for the DoD/DOE/EPA Strategic Environmental Research and Development Program (SERDP), that an important aspect of modeling kinetics in supercritical water is the extent to which neighboring water molecules participate in the formation of activated complexes. Theoretical predictions of the role of high-density water in the homogenous gas-phase water-gas shift mechanism made by Carl Melius and co-workers indicate that, at sufficiently high water densities, the activation energies for formation of both the intermediates and products are significantly reduced by the participation of additional water molecules in the transition state complex.

This theoretical prediction is illustrated in Figure 1, showing the reaction pathway for the formation of formic acid from CO and water. With the extra water molecule, the transition state is much less strained and more polar, resulting in a lower activation energy and greater electrostatic stabilization by water solvation.

Figure 2 shows experimental measurements of the water-gas shift reaction for a range of pressures at 450°C employing Raman spectroscopy as an *in situ* real-time diagnostic. A full set of data has been obtained over temperatures ranging from 410°C to 520°C and water density ranging from 1 to 35 mol/liter. Clearly, there is a very rapid change in the rate of the conversion of CO to CO_2 for a relatively small change in the density of supercritical water, over the pressure range of 41 to 59 MPa.

Reactions in supercritical fluids are known to exhibit unusual behavior near the critical point of the solvent. The data at 410°C are used to determine the effective volume of activation $\Delta V^{\ddagger} = $ -1135 cm^3/mol. This result is in excellent agreement with the theoretical prediction of -1178 cm^3/mol. The large negative volume of activation at conditions near water's critical density shows the profound effect that the high compressibility of a supercritical fluid can have on reaction rates when the activated complex possesses electronic structure characteristics very different from the reactants.
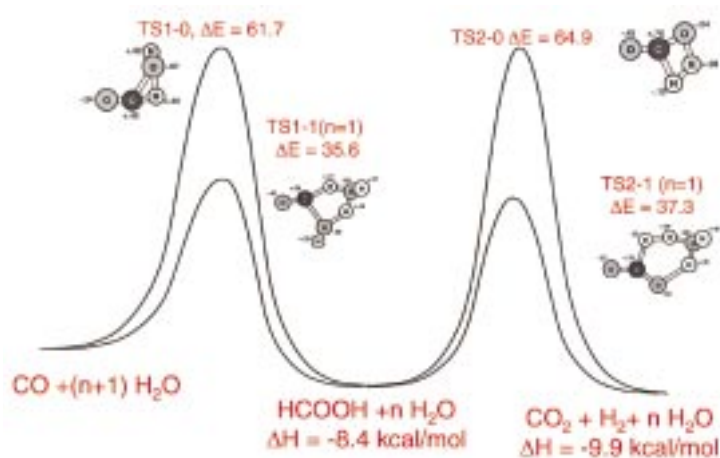

Figure 1. The energy associated with the activated complex in the water-gas shift can be significantly changed by the presence of an additional water molecule. Water can also stabilize these complexes through solvent-like electrostatic forces.
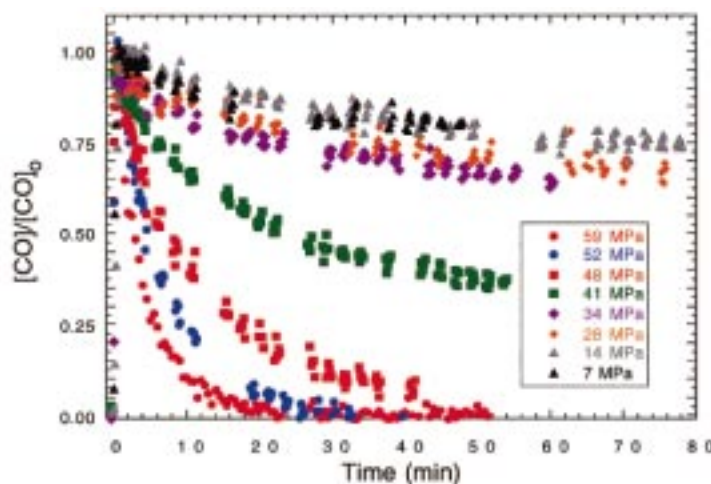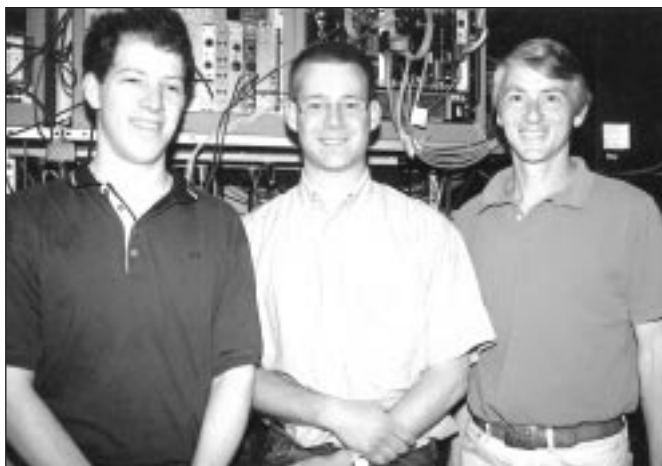

Figure 2. Observed concentration of CO reacting in supercritical water at 450 °C for a range of pressures. All the data were recorded with an initial CO concentration of approximately 0.15 mol/l.

Pieter Nooren (center) of the Technical University of Delft completed a three-month visit in the Turbulent Diffusion Flame laboratory, where he worked with Rob Barlow (right) and Jonathan Frank (left) to obtain multiscalar measurements in piloted jet flames of natural gas.

Eric Croiset (right) from CNRS Orléans, France, has just completed a visit with Steve Rice during which he worked on reaction kinetics in supercritical water.

Markku Orjala (second from right) from VTT Technology in Finland completed a six-month visit at the Multifuel Combustor lab. During his visit he investigated biomass combustion with (from left) Steve Buckley, Larry Baxter, and Allen Robinson.

Ahmed Ghoniem of MIT recently completed a sabbatical at the CRF. He worked with Habib Najm on the development and validation of flame models, including detailed chemical kinetics and unsteadiness, in two-dimensional vortical flow.

The CRF II project has recently completed two major milestones in the construction process. "Beneficial occupancy" of the new office wing (Bldg. 905) was accomplished on schedule on April 30, 1997. Office equipment began arriving in May and June, and occupancy is scheduled for early July.

Meanwhile, bids were received and a contractor was selected in early May for the construction and outfitting of the first four laboratories in Bldg. 906. These efforts are expected to be completed in June 1998 with follow-on contracts planned for outfitting the remaining CRF II labs.

HCO identified as a reliable measure of flame heat release

Habib Najm and Phillip Paul, working with Charles Mueller and Peter Wyckoff, have recently identified the formyl radical, HCO, as a reliable flame marker with excellent correlation with heat release and burning rates in premixed methane-air flames.

HCO plays a key role in the oxidation of hydrocarbons in combustion processes. It is formed via decomposition and abstraction reactions with formaldehyde, CH_2O, and promptly reacts with almost every other partner in the flame to yield CO plus radicals. Its utility as a burning/heat release rate measure is due to both its fast dissociation and the fact that most of the carbon travels down the path leading through HCO to CO and CO_2.

The correlation between HCO and burning/heat release rate was identified using numerical computations of the interaction of a premixed methane-air flame with a counter-rotating vortex pair, using detailed C_1 chemical kinetic mechanisms (see *CRF News* **18**:6, p. 4).

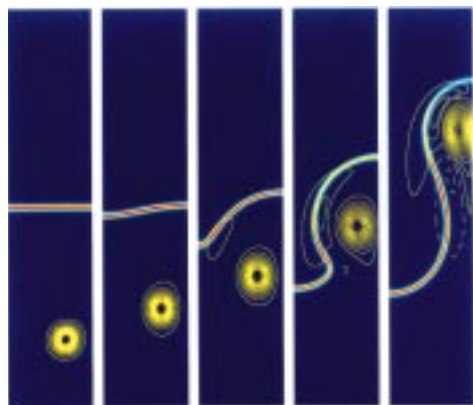A typical interaction sequence is shown in Figure 1, where the heat-

Figure 1. Time sequence illustrating computed flame interaction with the counter-rotating vortex pair, using 0.4 x 1.8 cm frames. The vertical right-hand-side edge of each frame is the centerline of the vortex pair, only half of which is computed. The time span is from 0 to 4 ms, left to right, with an interval between adjacent frames of 1 ms. The color map indicates head release rate. The solid/dashed contours delineate levels of positive/negative vorticity, where positive vorticity corresponds to counter-clockwise fluid rotation. The vortex pair is initialized in the reactants.

release rate is plotted superposed on the vorticity field contours, for a flow time span of 4 ms. The data indicate the drop in heat release rate at the centerline of the vortex pair as it propagates into the flame.

The variation of peak HCO mole fraction along the flame, at time 3 ms, is plotted together with heat release and methane burning rate peaks in Figure 2. These data show the remark-
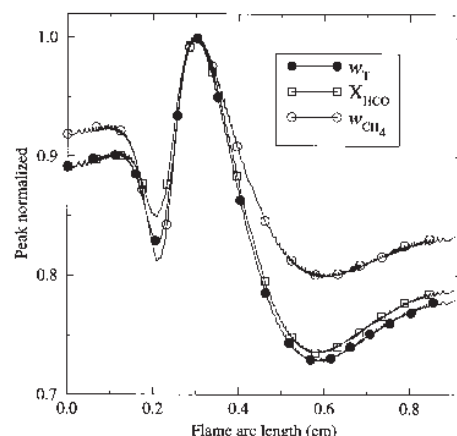

Figure 2. Peak heat release rate w_T, HCO mole fraction X_{HCO}, and CH_4 consumption rate w_{CH_4}, plotted against flame arc length, measured from the flame segment at the left edge of the computational domain, at time 3 ms. Each quantity is normalized with respect to its maximum value along the flame.

able spatial correlation observed for HCO. Temporal correlation with burning/heat release rate is equally good.

The number density of HCO was also measured using Planar Laser-Induced Fluorescence (PLIF) imaging. The experiment investigated the interaction of an isolated vortex pair with a premixed V-flame (see *CRF News* **18**:6, p. 1). The PLIF was performed using excitation near 258.4 nm, corresponding to an overlap of HCO B-X(0,0,0) $^QR_0(9)$ and $^QR_0(7)$ transitions, with detection of the strongly red-shifted fluorescence.

Because of the relatively low concentration of HCO, its PLIF imaging is extremely challenging. It was necessary to frame average, and to take special care to reject natural flame emission and avoid excitation of other species. An HCO PLIF image is shown in Figure 3, taken in a stoichiometric methane air flame, indicating an uninterrupted flame surface. This is in contrast to a CH PLIF image, taken under
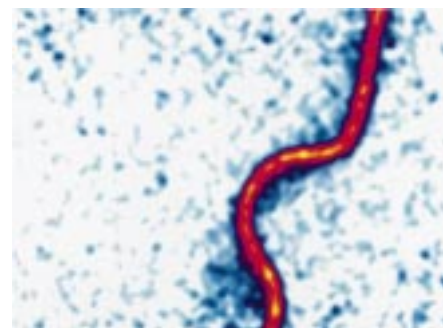

Figure 3. PLIF image of HCO. The field of view is 2.8 by 2 cm with the products on the left and reactants on the right. The vortex pair was injected at a near normal angle to the flame surface. The overall flow is vertical with a free stream velocity of 42 cm/s. The color table is linear running from white (low) to blue to red to yellow (high).

the same conditions, showing a complete break in the CH surface around the vortices.

Further work is in progress on more detailed computations using C_1-C_2 kinetics spanning ranges of stoichiometry and on time-resolved PLIF measurements of HCO to evaluate its utility as a flame marker over wider ranges of flow and flame parameters. ✍

Trace chemicals analyzed using fast chromatographic separations

For almost four years, scientists now affiliated with Sandia's new Chemical and Radiation Detection Laboratory have developed and applied a variety of chemical analysis techniques based on electrokinetically driven capillary separation techniques. Recently, Deon Anex and Gary Hux, in collaboration with Rajeev Dadoo and Richard Zare (Stanford University) and Chao Yan (Unimicro Technologies, Inc.), have performed chemical analyses in under five seconds using extremely fast capillary separations coupled with laser-induced fluorescence (LIF) detection.

The research team used a high-resolution chemical separation technique known as capillary electrochromatography (CEC). In CEC, an electric field is used to drive a fluid (the mobile phase) through a fused silica capillary column; these columns are hollow capillary tubes that typically have an inner diameter of about 100 micrometers packed with small silica particles. A coating on the particles (the stationary phase) causes a chemical sample to separate into its component bands as it passes through the column. The separated bands are detected using LIF as they pass from the column and are identified by their characteristic elution time from the column. Laser-based techniques such as LIF allow sensitive detection of trace chemical species.

To achieve expected gains in column separation efficiency when smaller particles are used, the researchers packed columns with 1.5 micrometer diameter particles. These columns can be made shorter than those packed with larger particles, which enables faster separations or lower voltage operation. Using longer columns packed with small particles results in very high efficiency separations.

An example of a separation using a short (6 centimeter) column is shown in the figure. By applying a high voltage (28,000 volts), the researchers have achieved very fast separations (under five second analysis time) without loss of efficiency. Five polycyclic aromatic hydrocarbons (PAHs), which are significant environmental pollutants, are analyzed in this example.

These results are extremely promising as enabling technology for a field-portable device, where either fast analysis or lower voltage operation is needed. Very fast CEC analysis will also have future applications in process monitoring and control. The demonstrated analysis in a short column indicates that similar columns will be useful when they are incorporated into future microfabricated chemical analysis devices now being developed at Sandia. ✎
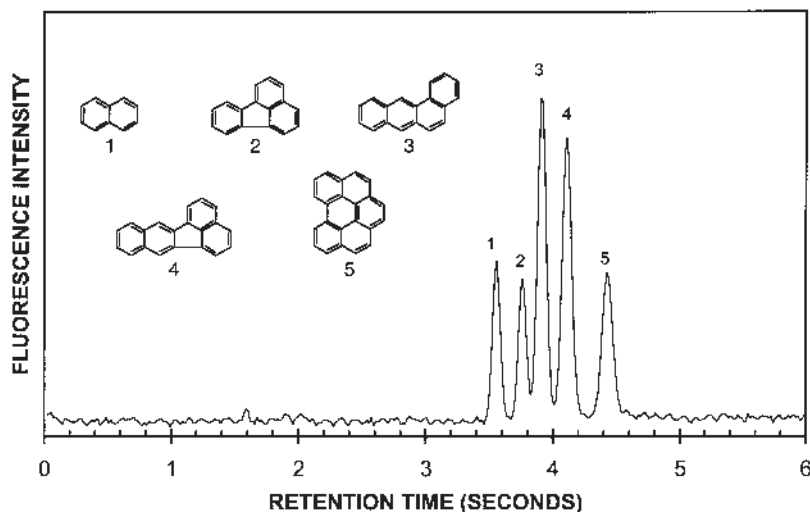
Capillary electrochromatogram showing the fast separation of five of the sixteen PAHs identified by the U.S. Environmental Protection Agency as priority pollutants. The species were detected by their native fluorescence in the wavelength range 280 to 600 nm after laser excitation at 257 nm.

The 1997 Sandia Combustion Research Technical Review is now available on the CRF Website at http://www.ca.Sandia.gov/CRF/Publications/SCRTR.